

Argonne National Laboratory

LABORATORY INVESTIGATIONS IN SUPPORT OF FLUID BED FLUORIDE VOLATILITY PROCESSES

Part IV. The Fluid Bed Fluorination of U_3O_8

by

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J. Fischer, J. J. Stockbar, J. G. Riha,
T. D. Baker, and G. W. Redding

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ANL-6763
Chemical Separations Processes
for Plutonium and Uranium
(TID-4500, 24th Ed.)
AEC Research and
Development Report

ARGONNE NATIONAL LABORATORY
9700 South Cass Avenue
Argonne, Illinois 60440

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Chemical Engineering Division

October 1963

Part I of this series is ANL-6742
Part II of this series is ANL-6753
Part III of this series is ANL-6762

Operated by The University of Chicago
under
Contract W-31-109-eng-38
with the
U. S. Atomic Energy Commission

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ABSTRACT

In one of the processes under development, the uranium and plutonium content of a spent reactor fuel of the Dresden type would be fluorinated in a fluid-bed reactor to produce the volatile uranium and plutonium hexafluorides. The study of the fluorination of U_3O_8 was undertaken because it is the major product obtained in an oxidative decladding step that is being proposed for the removal of uranium and plutonium from stainless steel-clad and Zircaloy-clad fuel elements. The study will also provide data needed for the development of apparatus and procedures for future work with mixtures of uranosic oxide and plutonium dioxide.

Experiments were performed to determine the optimum reaction conditions for the conversion of U_3O_8 to uranium hexafluoride and for minimizing the elutriation of unreacted U_3O_8 from the fluid bed. Elutriation of U_3O_8 from the fluid bed was minimized when a fluid bed height of 8 in. of 120 mesh alumina, a fluorinating gas phase containing 20 v/o fluorine, and a reaction temperature of 500 C were employed. Conversion of greater than 99 percent of the U_3O_8 to uranium hexafluoride was obtained when the feeding-fluorination period, in which the U_3O_8 powder was fed into the fluid bed and the major part of the fluorination was accomplished by reacting the oxide with 20 v/o fluorine, was followed by a recycle-fluorination period of 5 hr at 500 C with 100 percent fluorine.

Kinetic data for the fluorination of U_3O_8 , obtained by means of a thermobalance, are reported for the temperature range from 300 to 400 C. The data were treated by the diminishing-sphere model. Experimental results are also presented for the oxidative decladding of stainless steel-clad and Zircaloy-clad uranium dioxide pellets.

*Affiliate, Institute of Nuclear Science and Engineering.

**Appointee, from Atomic Energy Commission, France.

I. INTRODUCTION

In the conceptual flowsheet of a fluid-bed fluoride volatility process,⁽¹⁾ the uranium and plutonium content of spent oxide fuels will be recovered by fluorination to produce the volatile hexafluorides of uranium and plutonium. The process will employ a fluid-bed reactor as the fluorination vessel and will use alumina as the fluidized medium. One of the schemes that is being considered for the decladding of the spent fuel employs an oxidation step to separate the uranium dioxide and plutonium dioxide from the stainless steel cladding or Zircaloy cladding as a mixture of U_3O_8 and plutonium dioxide. The oxide mixture produced by this oxidation process is a finely divided, free-flowing powder. This was shown in experiments performed to test the efficacy of the oxidative decladding technique (see Appendix A).

Two alternative schemes have been proposed for carrying out the combination of oxidation and fluorination reactions. In one, the oxidation and fluorination steps would be performed in the same fluid-bed reactor. The oxidation of the spent oxide fuel would be performed in the lower section (oxidation zone) of the fluid bed. The U_3O_8 fines formed in the oxidation zone would be transported to the upper section (fluorination zone) of the fluid-bed reactor by the oxidizing gas stream. In the fluorination zone, the oxide fines are fluorinated by means of fluorine which is introduced into the reactor at a point just above the oxidation zone. The second scheme would employ a separate oxidation reactor and the oxide powder formed would be fed into the fluid bed of the fluorination reactor by gas transport in a nitrogen stream used to fluidize the bed.

In previous laboratory work on process development, removal of plutonium from mixtures of alumina, uranium dioxide, plutonium dioxide, and fission product element oxides by fluorination at 450 to 550 C had been studied. These studies, which were described in the first report in this series,⁽²⁾ indicated that plutonium removal from the Alundum bed could be increased by oxidizing mixtures containing uranium dioxide-plutonium dioxide solid solutions to U_3O_8 -plutonium dioxide mixtures before fluorinating the mixtures.

In the experimental work described herein, the second reaction scheme, in which the uranium dioxide was first oxidized in a separate vessel and then fed into the fluid-bed fluorinator, was used. A prototype fluid-bed fluorinator was set up for use with uranium alone in order to test and develop apparatus and procedures for subsequent work with plutonium dioxide- U_3O_8 mixtures. Fluorination experiments were performed to determine the optimum conditions of temperature, U_3O_8 powder feed rate, and reaction time for conversion of the U_3O_8 to uranium hexafluoride. Ancillary experimental work was performed on the oxidative removal of uranium dioxide pellets from stainless steel and Zircaloy cladding (see Appendix A) and on the kinetics of the reaction between U_3O_8 and fluorine (see Appendix B).

II. EXPERIMENTAL

1. Materials

The U_3O_8 used in this work, obtained from Union Carbide Nuclear Company, had a surface area of 0.74 sq m/g, as measured by nitrogen adsorption, and an average particle diameter of 3.1 μ . Chemical analysis of the U_3O_8 indicated a uranium content of 84.46 percent (theoretical content: 84.80 percent). Spectrochemical analysis indicated that the principal contaminants of the oxide, expressed in ppm, were: Al, 30; Cr, 10; Fe, 50; Mo, 30; Ni, 50; and Si, 30. Commercial-grade fluorine, which was passed through a sodium fluoride trap at 100 C to remove hydrogen fluoride, was used. The nitrogen, which was used as the fluidizing gas and also as a diluent for the fluorine, was passed through a trap containing molecular sieves to remove water. High-purity fused alumina was employed as the inert fluidized material.

2. Apparatus

The fluorination apparatus consisted of the following major components: (1) a 1 $\frac{1}{2}$ -in.-diameter fluid-bed fluorinator; (2) a powder feeder; (3) a system of cold traps to condense uranium hexafluoride; (4) a Lapp diaphragm pump employing a remote head to circulate the gas phase; (5) activated alumina traps for the disposal of fluorine; and (6) manifolds supplying fluorine, nitrogen, and vacuum service.

Figure 1 is a schematic representation of the fluid-bed fluorination reactor. The lower section, which contained the alumina bed, was fabricated from a 1-ft section of 1 $\frac{1}{2}$ -in.-diameter, schedule 40 nickel pipe. The upper section of the reactor, the disengaging chamber, was fabricated from a 1-ft section of 3-in.-diameter, schedule 40 nickel pipe, and contained two sintered nickel bayonet filters through which the reactor off-gases passed. A gas and solids distributor was located within the conical bottom of the lower reactor section. This device insured a uniform distribution of the uranous oxide powder in the fluid bed and provided an inlet for the fluorine-nitrogen mixture into the fluid bed above the entry point of the oxide powder.

Tests showed that satisfactory fluidization of the solids and distribution of the gas were accomplished when the fluidizing gas and U_3O_8 entered the bed through an annular inlet, approximately half the diameter of the reactor. The annulus was provided between the conical bottom of the reactor and the double-cone gas-solids distributor, as shown in Figure 2. Small metal spacers, attached to the bottom of the gas-solids distributor, were interposed between the distributor and the conical bottom of the reactor. Fluorine entered the distributor by means of a central tube connected to the bottom of the distributor, and the gas then entered the bed through eight holes located in the upper portion of the distributor. Twenty grams of

powder, having an average particle diameter of 6μ , could be fed in 1 min into a 5-in.-high alumina bed composed of 60 mesh particles. The flow rate of the fluidizing gas was approximately 0.5 cfm at room temperature.

Figure 1

FLUID-BED FLUORINATION REACTOR

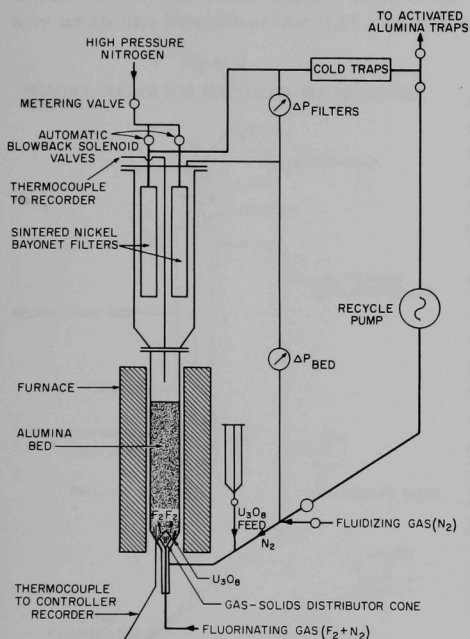
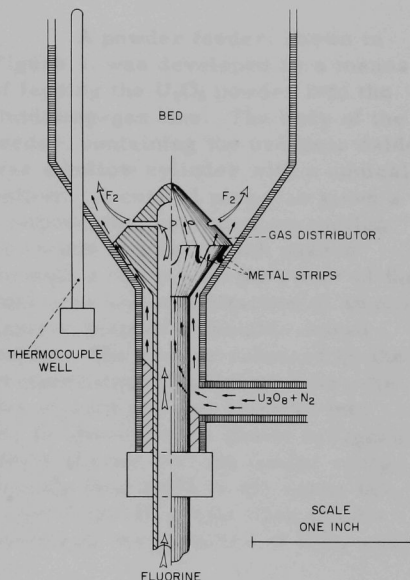


Figure 2

GAS-SOLIDS DISTRIBUTOR FOR 1-1/2-IN. FLUIDIZED-BED REACTOR



108-6288

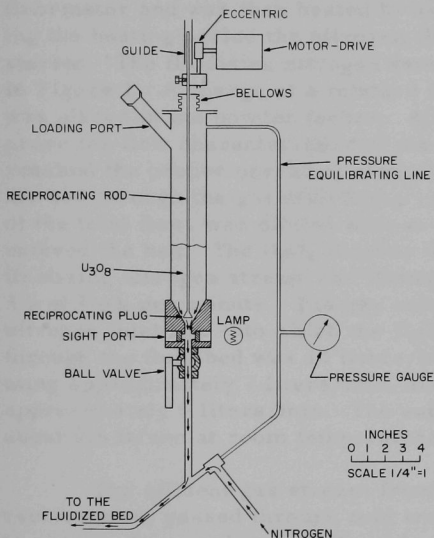
The reactor was heated by a resistance furnace which had three heating elements. The two lower elements were controlled by a thermocouple inside the reactor at the level of the fluorine inlet, whereas the upper element was controlled by a thermocouple placed at about the middle of the outside surface of the reactor.

An automatic blowback system, described by Loeding *et al.*,⁽³⁾ was employed to return solids which reached and were retained on the surface of the sintered nickel filters. A Venturi throat and jet were used in this system to deliver a high-speed flow of nitrogen through the bayonet filter countercurrently to the normal gas flow of the system. Since the blowback procedure was alternated between the two filters, no interference with the normal flow of the reaction gases resulted.

The cold-trap system used to condense the uranium hexafluoride consisted of three traps in series. The traps were refrigerated at about -80°C by use of a carbon dioxide-trichloroethylene slush. The traps were 4 in. in diameter and 1 ft in length. In the second and third traps a sintered nickel bayonet filter was placed on the outlet line of the gas stream to retain any particulate matter. A trap packed with sodium fluoride was placed in series after the cold traps. This trap, which was heated to 100°C , sorbed any uranium hexafluoride that had not condensed in the cold traps.

Figure 3

POWDER FEEDER FOR FLUIDIZED-BED REACTOR



A powder feeder, shown in Figure 3, was developed as a means of feeding the U_3O_8 powder into the fluidizing-gas line. The body of the feeder, containing the uranous oxide, was a hollow cylinder with a conical bottom. A conical plug was given a reciprocating up-and-down motion by means of a rod which passed through a bellows on the cover of the container and was attached to an eccentric shaft of a variable-speed motor. The powder released by the reciprocating plug dropped into the gas stream and was injected into the fluidized bed as shown in Figure 1. Tests showed that the feeder could provide feed rates in the range between 2 and 20 g/min when the diameter of the particles of U_3O_8 was $6\ \mu$.

The Lapp diaphragm pump, used to recirculate the fluorine, had a rated flow capacity of 0.5 cfm at a discharge pressure of 15 psig and atmospheric pressure intake. The remote head of the pump is constructed of Monel and nickel on the gas pumping side, and the impulse is transmitted from the compression head by means of a transmission line filled with fluorolube oil. Measurements of flow rate were made by means of a thermal flowmeter of the type described by R. Kessie.⁽⁴⁾ Flow calibration of the pump-flowmeter combination was accomplished with nitrogen using a wet test meter.

3. Procedure

The fluorinations of U_3O_8 were performed in two reaction periods. In the first period, which will be referred to as the feeding-fluorination period, the U_3O_8 powder was injected into the fluid bed, and the major part

of the oxide was converted to uranium hexafluoride by means of a gas mixture of 20 v/o fluorine in nitrogen. In the second period, which will be referred to as the recycle-fluorination period, the fluorine content was raised to about 100 percent, and the gas recycled through the Lapp pump and back to the fluidized bed. The last traces of uranium were removed during the recycle-fluorination period. In future experiments with uranium dioxide-plutonium dioxide solid solutions, this step will serve to remove the plutonium from the bed material.

The general operating procedure for the fluorinations was as follows: About 400 to 500 g of 120 mesh fused alumina was placed in the fluid bed fluorinator and was then heated to the operating temperature of 500 C. During the heating period the nitrogen flow needed to fluidize the bed was started. The fluidizing nitrogen entered the bottom of the reactor as shown in Figure 1. A charge of a mixture of U_3O_8 and alumina in a 2:1 weight ratio was placed in the powder feeder. Alumina was mixed with the U_3O_8 to improve the flow characteristics of the oxide powder. When the reactor reached the proper operating temperature the fluorine flow was started into the bed through the gas distributor cone. The fluorine, which was 20 v/o of the total flow, was diluted with an equal quantity of nitrogen before it entered the bed. The U_3O_8 alumina mixture was then introduced into the fluidizing nitrogen stream and thence into the fluid bed at a rate of about 3 g of U_3O_8 per minute. The gas velocity in the $\frac{3}{8}$ -in.-diameter fluidizing nitrogen inlet line into which the U_3O_8 is fed was 5 ft/sec. Total flow rate through the fluid bed was 12 liters/min, with the fluidizing nitrogen contributing approximately 7 liters/min, and the mixture of fluorine and nitrogen approximately 5 liters/min. The superficial velocity in the fluid bed was about 0.6 ft/sec at room temperature.

The effluent gas stream from the fluorinator, when the gas is not recirculated, passed through cold traps and a sodium fluoride trap in order to remove the uranium hexafluoride, and then through an activated alumina trap which reacts with and removes excess fluorine. The effluent was then exhausted to the atmosphere. This once-through flow was continued while the U_3O_8 -alumina mixture was being fed into the fluid bed. In the cases in which no recycle was used, the once-through flow was continued for $\frac{1}{2}$ hr after the feeding was completed.

Following the feeding-fluorination period, the fluorine content of the gas phase was brought to approximately 100 percent and the recycle period was started. The recycle flow was carried out for a period of 5 hr. After the reaction period had been completed, the sodium fluoride trap and the cold traps, which were maintained at -78 C, were evacuated to remove the residual gas phase. The traps were then warmed to room temperature and weighed to assay the amount of uranium hexafluoride collected. The fluid-bed alumina was removed from the reactor and sampled for uranium analysis. The small amount of mixture of U_3O_8 and alumina which was retained in the disengaging section was removed and submitted for uranium analysis.

III. RESULTS AND DISCUSSION

In the first series of experiments, the parameters affecting the elutriation of U_3O_8 from the alumina bed were explored. The elutriation of U_3O_8 from the alumina bed results in the deposition of solids containing uranium on the surfaces of the disengaging chamber and filters, where no fluorination of the U_3O_8 occurs. For these experiments, the bayonet filters were removed from the disengaging chamber, and the solids which passed through the disengaging chamber were trapped in a filter that was placed in a separate outside chamber of the reactor. By weighing the filter before and after the experiment, the quantity of unreacted U_3O_8 and alumina elutriated from the fluid bed could be determined. A determination of the quantity of U_3O_8 elutriated was made by dissolving the U_3O_8 in the elutriated solids with nitric acid. The residual alumina was then dried and weighed, the weight of U_3O_8 being obtained by differences.

The results obtained in experiments in which the particle size of the alumina, the bed height, and fluorine concentration were varied are shown in Table 1. When the particle size of the alumina was decreased from 60 to 120 mesh, elutriation of U_3O_8 from the bed was reduced from 19.5 to 9.0 percent of the U_3O_8 fed to the bed. When a 50-50 mixture of 60 and 120 mesh alumina was used, the amount of U_3O_8 elutriated was not appreciably less than the amount elutriated when 60 mesh alumina was used.

Table 1

EXPERIMENTAL CONDITIONS AFFECTING ELUTRIATION OF U_3O_8 FROM A FLUIDIZED BED DURING FLUORINATION

<u>Experimental Conditions</u>				
Fluid-bed Alumina:		520 g		
U_3O_8 :		100 g		
Feed Rate U_3O_8 :		Approx. 3 g/min		
Bed Temperature:		500 C		
Total Gas Flow Rate ($F_2 + N_2$):		12 liters/min		
Superficial Fluidizing Gas Velocity:		1.6 ft/sec at 500 C		
Gas Velocity in $\frac{3}{8}$ -in.-dia Feed Line:		5 ft/sec at 25 C		
Reaction Parameter Varied	Al_2O_3 Particle Size (mesh)	Bed Height (in.)	F_2 Conc in Gas (v/o)	Percent Elutriation of U_3O_8
<u>Al_2O_3 Mesh Size</u>	120	8	20	9.0
	60	8	20	19.5
	60 + 120 ^a	8	20	19.0
<u>Bed Height</u>	120	4	20	23.0
	120	8	20	9.0
	120	12	20	9.5
<u>Fluorine Concentration</u>	120	8	10	29.0
	120	8	20	9.0
	120	8	30	5.7

^aMixture: 50 w/o 60 mesh alumina + 50 w/o 120 mesh alumina.

Variation of the height of the alumina bed also affected the amount of U_3O_8 elutriated from the bed. Increasing the bed height from 4 to 8 in. reduced the amount of U_3O_8 elutriated from 23 to 9 percent of the quantity of U_3O_8 charged to the bed, as shown by the results listed in Table 1. Further increase in bed height, however, did not result in a further reduction in the amount of U_3O_8 elutriated from the bed.

The amount of U_3O_8 elutriated from the fluid bed was found to decrease as the concentration of fluorine in the reactant gas was increased. As shown in Table 1, the concentrations of fluorine used were 10, 20, and 30 v/o. With these gas mixtures, the amounts of U_3O_8 elutriated were 29, 9.0, and 5.7 percent, respectively, of the amount of U_3O_8 originally present. From these data, it is apparent that the elutriation of U_3O_8 from the fluid bed will decrease with decreasing particle size of the alumina, increasing bed height, and increasing concentration of fluorine.

In a second series of experiments, the effect of temperature on the fluorination of U_3O_8 to uranium hexafluoride was examined. The bayonet filters were reinserted in the disengaging chamber, and each filter was subjected to a blowback with nitrogen every 5 min during the experiment. As in the earlier experiments, gas recycle was used except during the feeding-fluorination period. Table 2 lists the data obtained for experiments performed at 450, 500, and 550 C. The percentages of U_3O_8 converted to uranium hexafluoride were 92 percent at 450 C, 97.6 percent at 500 C, and 98.5 percent at 550 C.

Table 2

EFFECT OF TEMPERATURE ON THE FLUID-BED FLUORINATION OF U_3O_8

Experimental Conditions

Fluid-bed Alumina:	470 g (120 mesh)
Feed Material:	100 g U_3O_8 (325 mesh), 50 g Al_2O_3 (120 mesh)
Total Gas Flow Rate ($\text{F}_2 + \text{N}_2$):	12 liters/min at 25 C
Superficial Fluidizing Gas Velocity:	1.6 ft/sec at 500 C
Gas Velocity in $\frac{3}{8}$ -in.-dia Feed Line:	5 ft/sec at 25 C
Filters alternately blown back every 5 min.	
Fluorination continued for $\frac{1}{2}$ hr after feeding-fluorination step completed.	

U_3O_8 Feed Rate (g/min)	Bed Temperature (C)	% Conversion of U_3O_8 to UF_6 Based on UF_6 Collected
2.4	450	92.0
3.6	500	97.6
2.4	550	98.5

A final series of experiments was performed at 500 C in which a 5-hr recycle period with 100 percent fluorine and an automatic blowback system were employed. During the recycle period, the portion of the feed line immediately adjacent to the reactor was heated to 450 C to facilitate the fluorination of any U_3O_8 which might have remained in this area. The experimental conditions used and the results obtained in these experiments are listed in Table 3. The data show that 99 percent or more of the U_3O_8 can be converted to uranium hexafluoride by means of a fluid-bed fluorination under the reaction conditions used in these experiments. In one experiment, the 5-hr cycle period was performed at a temperature of 550 C;

Table 3
FLUID-BED FLUORINATION OF U_3O_8

<u>Experimental Conditions</u>						
Fluid-bed Alumina:		120 mesh, 420 g				
Uranosic Oxide-Al ₂ O ₃ Feed Mixture:		300 g U ₃ O ₈ ; 150 g Al ₂ O ₃				
Feeding-Fluorination Period:						
Bed Temperature:		500 C				
Total Gas Flow Rate (at 25 C):		12 liters/min				
Fluidizing N ₂		7 liters/min				
Fluorine		2.5 liters/min				
N ₂ in Fluorine		2.5 liters/min				
Superficial Fluidizing Gas Velocity:		1.6 ft/sec at 500 C				
Gas Velocity in $\frac{3}{8}$ -in.-dia Feed Line:		5 ft/sec at 25 C				
Recycle Period:						
Bed Temperature:		500 C				
Total Gas Flow Rate:		8 liters/min				
Fluorine Conc in Gas Phase:		100 percent				
Recycle Time:		5 hr				
Temperature of Feed Line:		450 C				
<u>Analytical Results</u>						
U ₃ O ₈ Feed Rate (g/min)	F ₂ Conc in Gas Phase during Recycle (v/o)	Total Residual U (g)	U in Al ₂ O ₃ Bed (g)	% U ₃ O ₈ Converted to UF ₆ Based on		Material ^b Balance (%)
				U ₃ O ₈ Residue ^a Unreacted	UF ₆ Collected	
3.7	100	0.26	0.12	99.7	99.8	100.1
3.7	100	0.37	0.24	99.9	98.9	99.0
2.5	100	0.77	0.09	99.8	99.0	99.2
3.5	100	2.28	0.26	99.5	98.5	99.0
5.1 ^c	100	0.13	0.07	100	101	101
4.1	100	0.63	0.24	99.8	97.6	97.8
4.6	100	0.82	0.09	99.7	100	100.3
6.0	100	0.99	0.30	99.6	99.5	99.9
5.9	50	0.57	0.39	99.7	99.2	99.5
3.8	50	0.60	0.11	99.7	99.1	99.4

^aMaterial retained in disengaging chamber and representative sample of bed material analyzed for uranium content, and the total uranium content from both of these sources used to calculate the percent conversion.

^bMaterial Balance % = % converted (UF_6 base) + [100 - % converted (Anal base)].

^cBed temperature during recycle fluorination period; 550 C.

at this temperature essentially complete conversion of the U_3O_8 to uranium hexafluoride was achieved. In two experiments the gas phase during the recycle-fluorination period contained 50 v/o fluorine. The conversion obtained in these experiments was essentially the same as that achieved in experiments with 100 percent fluorine.

The higher values of conversion listed under Column 5 in Table 3 are based on the results of analyses for uranium of representative samples of the bed material and the material deposited in the disengaging chamber. Uranium retention in the alumina beds ranged from 0.02 to 0.05 w/o, corresponding to 0.1 to 0.3 g of uranium for total weights of the recovered alumina beds of from 518 to 572 g. The disengaging chamber samples, which ranged in weight from 1 to 3 g, contained from 0.1 to 1.0 g of uranium. The total uranium contents of the alumina beds and disengaging chamber samples represented 0.1 to 0.5 percent of the uranium fed to the reactor. The material balance figures were calculated from the percent conversion figures based on uranium hexafluoride collected and the analyses of the bed and disengaging chamber material as follows:

$$\text{Material Balance } \% = \%(\text{UF}_6 \text{ base}) + [100 - \%(\text{Anal base})].$$

The somewhat lower conversion figures based on uranium hexafluoride collected are apparently not due to loss of hexafluoride, since the quantities found on the sodium fluoride were well below the tested capacity of the trap. It is probable that the discrepancy is due to weighing inaccuracies.

The results obtained in this work showed that greater than 99 percent of the 100 g of U_3O_8 powder fed to a fluid bed under the reaction conditions used in this study can be converted to uranium hexafluoride. The experimental conditions (shown in Table 3) which were developed during the course of this study will serve as the initial reaction conditions for future work in which mixtures of U_3O_8 and plutonium dioxide will be fluorinated.

The high conversions to uranium hexafluoride and the small amounts of U_3O_8 found in the disengaging chamber of the reactor indicate that the U_3O_8 must be reacted in the narrow zone in which the U_3O_8 and fluorine mix. That U_3O_8 reacts rapidly with fluorine was shown by kinetic experiments performed over the temperature range from 300 to 400 C (see Appendix B). A reaction rate of 0.02 g of U_3O_8 per minute at 400 C was obtained. From the extrapolated reaction rate at 500 C, a reaction time for a particle of U_3O_8 of 1.7 min was calculated. An estimate made of the residence time of a particle 12μ in diameter in a fluid bed at a superficial gas velocity of 0.67 ft/sec is 24 min.⁽⁵⁾ Therefore, the particles should be reacted completely in the bed, and the conversion obtained in this work tend to substantiate this conclusion.

IV. APPENDIX A

Oxidative Decladding of Stainless Steel-clad and
Zircaloy-clad Uranium Dioxide Pellets

Removal of uranium dioxide and plutonium dioxide from stainless steel cladding by oxidation of the uranium dioxide to U_3O_8 is being considered as a step which would precede fluorination in a fluid-bed fluoride volatility process. Oxidation of uranium dioxide pellets results in an increase in volume and pulverization of the pellets as U_3O_8 is formed. The feasibility of the process was demonstrated at Atomics International,⁽⁶⁾ where successful decladding of uranium dioxide pellets clad in Type 304 stainless steel was achieved by oxidation at 400 to 500 C with air or oxygen. In these experiments, in which greater than 99 percent of the uranium dioxide was removed from the cladding by oxidation, holes were punched through the cladding at short intervals along the length of the fuel elements. This procedure resulted in the rupture of the cladding during oxidation, thus allowing greater access of the oxidizing gas to the uranium dioxide pellets. The U_3O_8 was separated from the cladding by mildly vibrating the assemblies.

In Appendix A, the oxidative decladding of uranium dioxide fuel elements in a fluid-bed reactor is discussed. The oxidative decladding step not only serves to separate uranium and plutonium oxides from the cladding material, but also serves to produce a uniform feed for the fluidized-bed fluorinator. Fluorination of spent uranium dioxide reactor fuel containing cracked and fragmented pellets results in uneven fluorination conditions if the fluorination is not preceded by oxidation. If oxidation does precede fluorination, finely divided U_3O_8 powder with an average particle size of $10\ \mu$ and surface areas of 0.5-1.0 sq m/g is produced, and the subsequent fluorination proceeds smoothly.

Introduction of the powdered U_3O_8 to the fluid bed fluorinator can be achieved by either of two methods. In one procedure, a section of the spent fuel elements is oxidized and declad in the lower section of the fluid-bed reactor, and the U_3O_8 and plutonium oxide powders are transported into the upper section of the fluid bed, where they are fluorinated. In an alternative procedure, the oxidized mixture of uranium and plutonium oxides are mechanically fed to the fluid-bed reactor.

Preliminary experiments in a horizontal tube furnace with $\frac{3}{4}$ -in.-long fuel sections which contained UO_2 pellets clad in Type 304 stainless steel tubing (wall thickness, 20 mils) showed the following results:

a) Complete conversion of UO_2 to U_3O_8 occurred in 3 to 4 hr at temperatures between 450 C and 550 C in a flowing stream of air; finely divided, freely flowing oxide powders were produced.

b) The oxidized material could easily be removed from the cladding tube by gentle vibration of the fuel elements.

c) Although oxidation is slightly faster at temperatures of 450 or 550 C in a stream of pure oxygen, the material has a tendency to cake and stick to the cladding.

Further work was carried out in a fluidized bed of alumina with UO_2 pellets clad in $5\frac{1}{2}$ -in.-long sections of Type 304 stainless steel or in Zircaloy. Slots ($\frac{1}{8}$ in. \times $\frac{1}{32}$ in.) were milled along the length of the cladding tubes with separations of $\frac{3}{8}$ in. between the ends of the slots. The wall thicknesses of the Type 304 stainless steel were 10 to 20 mils, and the thickness of the Zircaloy cladding was 30 mils. The experiments were performed at 450 C, with dry air as the fluidizing and oxidizing gas. A single run, in which the UO_2 pellets were clad in Type 304 stainless steel tubing having a wall thickness of 20 mils, was carried out at 550 C with air as the oxidant. The results of these experiments are given in Table 4. In all cases an initial swelling of the cladding tube was followed by a partial and then complete splitting of the cladding along the slit line. With 10- and 20-mil-thick stainless steel cladding, the tubing split open along its entire length after 2 and 4 hr of oxidation, respectively. Complete removal of the U_3O_8 product was accomplished by oxidizing for an additional 1 or 2 hr. In the experiment at 550 C, 20-mil-thick stainless steel was completely split after 6 hr of oxidation. The different stages of the splitting of the cladding are shown in Figure 4. The cladding shown in Figure 4 was stainless steel with a wall thickness of 20 mils.

Table 4

OXIDATIVE DECLADDING OF UO_2 PELLETS CLAD IN
TYPE 304 STAINLESS STEEL OR ZIRCALOY

UO_2 Pellets: NUMEC, size: $\frac{7}{16}$ -in. dia, $\frac{7}{16}$ -in. length
Fluid-bed Material: 500 g of 120 mesh Al_2O_3 (Norton Co.)
Fluidizing Gas: Air (linear velocity, 0.3 ft/sec at 25 C)
Size of Clad Pins: $5\frac{1}{2}$ -in. long, with $\frac{1}{8}$ -in. \times $\frac{1}{32}$ -in. slots
milled along the length with a $\frac{3}{8}$ -in.
spacing between ends of slots.
Number of Pellets: 12; total wt UO_2 , ~120 g.

Temperature (C)	Type and Wall Thickness of Cladding (mils)	Percent Retention ^a of UO_2 in Cladding with Time (hr)								Average Rate of Removal (g/hr) ^b
		1	2	3	4	5	6	7	8	
450	SS, 10	-	65.7 ^c	-	0.02	-	-	-	-	30 ^d
450	SS, 20	-	93.4	-	18.2 ^c	0.03	-	-	-	24 ^d
450	Zircaloy, 30	-	98.6	-	87.2	-	10.0 ^c	-	0.15	15 ^d
550	SS, 20	-	91.4	-	91.1	-	10.0 ^c	0.03	-	17 ^e

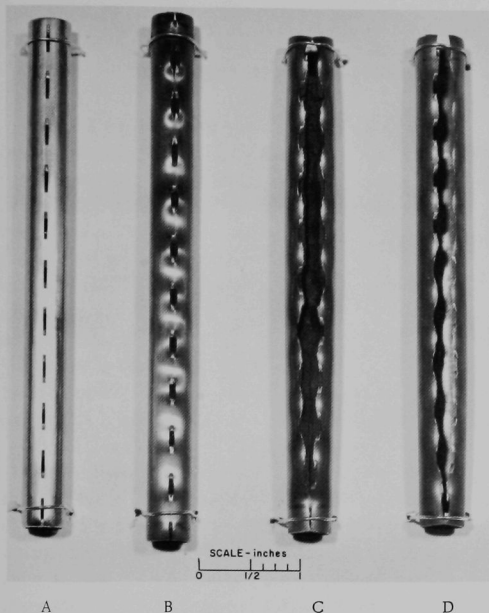
^aCalculated on basis of initial weight of UO_2 .

^bCalculated using time necessary for complete removal of oxide from cladding.

^cClad tube split open completely at the end of this period.

^dFine powders of oxidized material in bed.

^eSlight caking of material observed.



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Figure 4
PHOTOGRAPH SHOWING TYPE 304 STAIN-
LESS STEEL-CLAD URANIUM DIOXIDE
FUEL ELEMENTS AFTER VARIOUS
STAGES OF OXIDATION

- A - Original Element, 20-mil-thick Type 304 stainless steel cladding.
B - Cladding after 2 hr of oxidation.
C - Cladding after 4 hr of oxidation.
D - Cladding after 5 hr of oxidation.

In Figure 4, A is the original element, B is a similar specimen after 2 hr of oxidation, C is a specimen after 4 hr of oxidation, and D is a specimen after 5 hr of oxidation and complete removal of the uranous oxide powder. Several observations can be made from the results of these experiments:

1) Oxidative decladding of uranium dioxide pellets clad in Type 304 stainless steel or Zircaloy is feasible in a fluid bed at 450 C, with air as the oxidant.

2) Milling slots along the length of the cladding allows greater access of the oxidizing gas to the pellets, promotes splitting of the cladding along the slot line, and makes easier the removal of U_3O_8 from the cladding.

3) The time necessary for complete removal of the U_3O_8 formed appears to be dependent on the time necessary to achieve complete splitting of the cladding, which in turn appears to be dependent on the thickness of the cladding.

V. APPENDIX B

The Kinetics of the Fluorination of Uranosic Oxide

The oxidative decladding of uranium dioxide fuel elements will produce finely divided, powdered U_3O_8 . In the fluid-bed fluoride volatility process, the U_3O_8 will be fluorinated in a fluid-bed reactor. The U_3O_8 will either be produced in the same fluid bed in which the fluorination will be carried out, or prepared in a separate reaction vessel and injected into the fluid bed of a fluorinator. It is necessary that the U_3O_8 be fluorinated during its residence time in the fluid-bed medium, in order to minimize elutriation of the U_3O_8 powder to cooler portions of the reactor, where reaction would not take place. A study of the kinetics of the reaction of fluorine with U_3O_8 was made in order to obtain information from which the residence time necessary to completely react a particle of U_3O_8 with fluorine in a fluid bed could be calculated.

Two batches of U_3O_8 were used in this study. The first, prepared by the New Brunswick Laboratory of the AEC and designated as NB-15, had a certified purity of 99.9+ percent. The second batch, prepared by Union Carbide Nuclear Corporation and designated as UCN, had a uranium content of 84.99 percent (theoretical for U_3O_8 , 84.80). The surface areas, as measured by nitrogen adsorption of the NB-15 and UCN source materials were 0.14 and 0.28 sq m/g, respectively. The fluorine used was commercial grade from which hydrogen fluoride was removed by passing the gas through a trap filled with sodium fluoride heated to 100 C.

The fluorination experiments were performed with a thermobalance that was specially designed for use with fluorine. The main components of this thermobalance, which has been described in detail by Johnson and Fischer,⁽⁷⁾ are a Sartorius Selecta analytical balance, equipped for automatic weight recording, and a vertical, tubular reaction chamber. A nickel sample pan, upon which the U_3O_8 powder was placed, was suspended in the reaction chamber by a Monel chain attached to the stirrup of the Sartorius balance. Fluorine was passed through a preheater before the gas entered the reactor. The flow rate of the fluorine was measured by a thermal flowmeter. A thermocouple positioned directly beneath the sample pan sensed the reaction temperature. The output of the thermocouple was measured with a Rubicon Type B potentiometer. A multipoint recording potentiometer was used to monitor the temperature of the furnace used for preheating the gas, the temperature of the reaction furnace, and the output of the thermal flowmeter.

In a typical experiment, 400 mg of U_3O_8 were placed on a tared nickel pan and then lowered into the reaction chamber which was preheated to the desired temperature. During this stage of the experiment, a flow of nitrogen was maintained through the reactor. The weight of the oxide sample was checked on the Sartorius balance while temperature equilibrium between gas

and solid was being attained. When the reaction system had reached a uniform temperature, the flow of nitrogen was stopped and a flow of fluorine at a rate of 150 cc/min was started. The weight change of the oxide sample versus reaction time was continuously recorded during the reaction period.

The data obtained in these experiments were correlated by use of the diminishing-sphere model. This treatment of the data has been discussed in detail by Johnson.⁽⁷⁾ Briefly, in the model it is assumed that in the gas-solid reaction, the solid reactant consists of spherical particles of uniform diameter, and that the reaction occurs uniformly on all the particles simultaneously, when the layer of solid is thin enough to allow saturation with the reactant gas. The reaction rate is then a function of the surface area of the particle. A mathematical treatment was developed for this kinetic model based on a gas-solid reaction occurring at a continuously diminishing spherical interface. In the final expression, the reaction rate is related to the fraction of unreacted solid as shown in the following equation:

$$(1 - F)^{1/3} = 1 - k't \quad , \quad (1)$$

in which

F = the fraction of solid reacted;

$k' = k/r_0\rho$, where r_0 is the initial radius of a particle, and ρ is the bulk density;

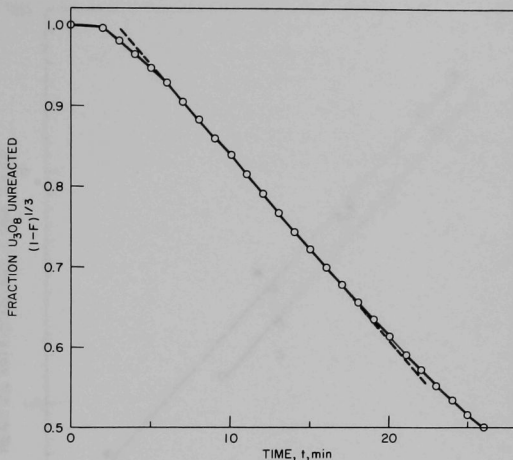
t = reaction time in minutes.

A plot of the function $(1 - F)^{1/3}$ versus t results in a straight line and the reaction rate constant can be obtained from the slope of the line.

Seven fluorination experiments with the UCN oxide and fourteen with the NB-15 oxide were performed in the temperature range from 300 to 400 C. The fluorinations required 2 hr or more at 300 C and about 20 min at 400 C. Plots of $(1 - F)^{1/3}$ versus time for each of the experiments resulted in straight lines over significant portions of the data. A plot for a typical experiment is shown in Figure 5. Deviation from the expected kinetics at the beginning of the experiment was due to dilution of the fluorine by the nitrogen initially present in the reactor. The deviation at the end of the reaction period was probably due to the small quantity of solid remaining. X-ray diffraction analyses of the residues indicated that uranyl fluoride is an intermediate in this reaction.

Figure 5
FLUORINATION OF U_3O_8

Temperature: 401 C
Fluorine Flow Rate: 120 ml/min
 U_3O_8 Mesh Fraction: -100 +325



Rate constants were calculated from the slopes of the plots of the function $(1 - F)^{1/3}$ versus time in minutes. The variation of these rate constants, k' of Equation (1), with temperature are shown in Figure 6 for experiments performed with samples of UCN and NB-15 oxides. From the slopes of the lines drawn through the two sets of data points, activation energies of 31 and 30 kcal/mole were calculated for the reactions between fluorine and NB-15 oxide and UCN oxide, respectively. The somewhat larger values of the reaction rate constants obtained with the UCN samples of U_3O_8 is probably due to the larger surface area of that material. The integrated form of the Arrhenius equation was fitted to the data to obtain the following equations representing the change in rate constant with temperature:

$$\text{NB-15 oxide, } \log k' = -\frac{6787}{T} + 8.4438 \quad ; \quad (2)$$

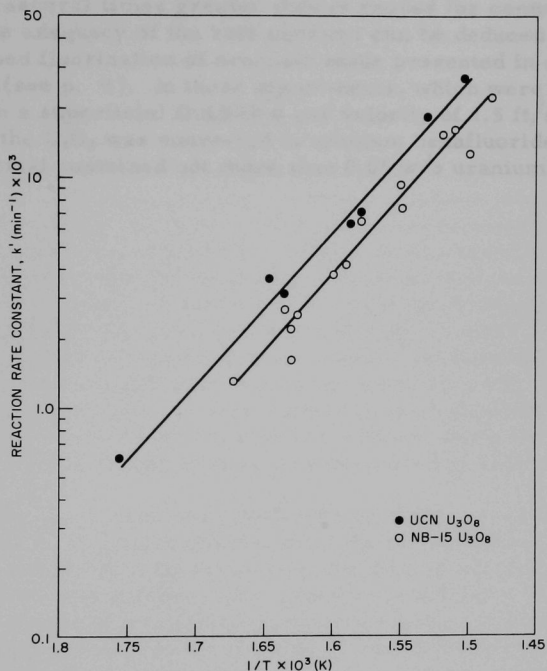
$$\text{UCN oxide, } \log k' = -\frac{6599}{T} + 8.3133 \quad . \quad (3)$$

Figure 6

VARIATION OF RATE CONSTANT, k' (min^{-1}), WITH TEMPERATURE FOR THE FLUORINATION OF U_3O_8

Temperature Range: 300-400 C

Rate Equation: $(1 - F)^{1/3} = 1 - k't$



By means of Equation (3), an extrapolated value of 0.6 min^{-1} was calculated for the rate constant at 500 C, the temperature for the fluid-bed fluorination of U_3O_8 . To estimate the time necessary completely to fluorinate a particle of U_3O_8 , the kinetic equation was used in the following form:

$$1 - \frac{r}{r_0} = k't \quad , \quad (4)$$

in which

r = radius of the particle at time t in the fluorination;
 r_0 = initial radius of the particle.

When r is very small, that is, when the particle has been essentially completely converted to uranium hexafluoride, then the time is equal to the reciprocal of the rate constant. The solution of Equation (4) for t , with the value for the extrapolated rate at 500 C, gave a value of 1.7 min. It has been calculated⁽⁵⁾ that the residence time of a 12- μ -diameter particle in a fluid bed at a superficial gas velocity of 0.67 ft/sec would be 24 min. Therefore, if the extrapolated rate constant is reasonably accurate, a residence time which is several times greater than is needed for complete reaction is available. The adequacy of the rate constant can be deduced from the data for the fluid-bed fluorination of uranosic oxide presented in another section of this report (see p. 9). In these experiments, which were performed at 500 C and with a superficial fluidizing gas velocity of 1.5 ft/sec, more than 99 percent of the U_3O_8 was converted to uranium hexafluoride; the alumina fluid bed material contained not more than 0.05 w/o uranium.

bed up to 1000 C. A fluidizing gas velocity of 1.5 ft/sec was used. The fluid bed was kept above the point at which the powder entered the bed. The periodic investigations of the effect of parameters such as temperature, U_3O_8 characteristics from the fluidized bed, and duration of the fluorination period upon the reaction. A scheme involving the fluorination of U_3O_8 at a temperature of 500 C has been developed. During the first period, U_3O_8 is fed into the fluid bed and fluorination is carried out simultaneously with 20 w/o fluorine in the gas phase. During the second period, a gas phase containing 50 percent fluorine is circulated through the fluid bed for a period of 5 hr. By means of this reaction scheme, more than 99 percent of the U_3O_8 fed to the fluid-bed reactor was converted to uranium hexafluoride.

Reaction rates have been measured by means of a thermobalance for the reaction of U_3O_8 with fluorine over the temperature range from 400 to 500 C. Two samples of U_3O_8 were used, one was an analytical standard sample, the other was commercially produced material. The data have been correlated by means of a diminishing square kinetic model which relates the reaction rate constant to the fraction of unreacted oxide. The reaction rate constants for the commercially produced material were slightly higher than those for the analytical standard sample, at the same temperatures. An average value of 30 kcal/mole has been calculated for the activation energy of the fluorination reaction which, within experimental error, was found to be the same for the two materials tested. Equations relating the change in reaction rate constant with temperature were derived. An estimate was made of the time required completely to convert a particle of uranosic oxide having a diameter of about 10 μ to uranium hexafluoride at 500 C. The estimate, which was based on an extrapolated value of the rate constant, resulted in a value of less than 2 min.

Two element mockups, which consisted of 2 $\frac{1}{2}$ -in.-diam sections of 1-in.-diameter stainless steel or zirconium, having cylindrical uranium dioxide pellets, were oxidized in a fluid bed at 400 C with air as the oxidant and fluidizing gas. Slats (1-in. x $\frac{1}{8}$ -in.) were inserted along the length of the cylindrical rods. At $\frac{1}{2}$ -in. intervals between the ends of the slats to represent the

VI. SUMMARY

In the conceptual flowsheet of the fluid-bed fluoride volatility process, the uranium and plutonium contents of spent oxide fuels will be recovered by fluorination to produce the volatile hexafluorides of uranium and plutonium. Laboratory-scale work has been concerned with the fluorination of U_3O_8 in a $1\frac{1}{2}$ -in.-diameter fluid-bed fluorinator, performed to develop and test apparatus and procedures for use in future work in which plutonium will be handled. The oxide U_3O_8 was used because it would be the major product obtained in an oxidative decladding step which has been proposed for the removal of uranium and plutonium from stainless steel- and Zircaloy-clad fuel elements.

In the present tests, the powdered U_3O_8 was injected into the fluid bed by means of a fluidizing nitrogen stream. Fluorine was introduced into the fluid bed just above the point at which the powder entered the bed. Experimental investigation of the effect of parameters such as temperature, U_3O_8 elutriation from the fluidized bed, and duration of the fluorination period upon the reaction. A scheme employing two fluorination periods at a temperature of 500 C has been developed; during the first period, U_3O_8 is fed into the fluid bed and fluorination is carried out simultaneously with 20 v/o fluorine in the gas phase; during the second period, a gas phase containing 100 percent fluorine is recirculated through the fluid bed for a period of 5 hr. By means of this reaction scheme, more than 99 percent of the U_3O_8 fed to the fluid-bed reactor was converted to uranium hexafluoride.

Reaction rates have been measured by means of a thermobalance for the reaction of U_3O_8 with fluorine over the temperature range from 300 to 400 C. Two samples of U_3O_8 were used; one was an analytical standard sample, the other was commercially produced material. The data have been correlated by means of a diminishing-sphere kinetic model which relates the reaction rate constant to the fraction of unreacted oxide. The reaction rate constants for the commercially produced material were slightly higher than those for the analytical standard sample at the same temperatures. An average value of 30 kcal/mole has been calculated for the activation energy of the fluorination reaction which, within experimental error, was found to be the same for the two materials tested. Equations relating the change in reaction rate constant with temperature were derived. An estimate was made of the time required completely to convert a particle of uranous oxide having a diameter of about $10\ \mu$ to uranium hexafluoride at 500 C. The estimate, which was based on an extrapolated value of the rate constant, resulted in a value of less than 2 min.

Fuel-element mockups, which consisted of $5\frac{1}{2}$ -in.-long sections of $\frac{1}{2}$ -in.-diameter stainless steel or Zircaloy tubing packed with uranium dioxide pellets, were oxidized in a fluid bed at 450 C with air as the oxidant and fluidizing gas. Slots ($\frac{1}{8}$ in. \times $\frac{1}{32}$ in.) were milled along the length of the cladding tubes at $\frac{3}{8}$ -in. intervals between the ends of the slots to promote the

splitting of the cladding during oxidation. The time necessary to split open a section of cladding along the slit line was dependent on the thicknesses of the tubing wall. In the case of stainless steel, tubes having wall thickness of 20 and 30 mils split open along their entire lengths after 2 and 4 hr of oxidation, respectively. In the case of 30-mil-thick Zircaloy, the tubing was completely split after 6 hr of oxidation. Complete removal of the U_3O_8 product was accomplished by means of 1-2 hr of additional oxidation.

VII. ACKNOWLEDGMENT

The authors wish to acknowledge the contribution of R. W. Kessie in the design and specification of the fluid-bed equipment used in this work.

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